

Theoretical prediction of topological insulator in ternary rare earth chalcogenides

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A new class of three-dimensional topological insulator, ternary rare earth chalcogenides, is theoretically investigated with *ab initio* calculations. Based on both bulk band structure analysis and the direct calculation of topological surface states, we demonstrate that LaBiTe_3 is a topological insulator. La can be substituted by other rare earth elements, which provide candidates for novel topological states such as quantum anomalous Hall insulator, axionic insulator and topological Kondo insulator. Moreover, YBiTe_3 and YSbTe_3 are found to be normal insulators. They can be used as protecting barrier materials for both LaBiTe_3 and Bi_2Te_3 families of topological insulators for their well matched lattice constants and chemical composition.

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Introduction- A topological insulator (TI) is a novel quantum state, which has attracted great attention in condensed-matter physics recently [1–3]. TIs in two or three dimensions have both insulating bulk energy gap and gapless edge or surface states on the sample's boundary. The surface states of three-dimension (3D) TIs consist of odd number of massless Dirac cones, which are protected by the time-reversal symmetry. TIs can be most generally defined as a new state of quantum matter whose effective electromagnetic action is given by the topological term $S_\theta = (\theta/2\pi)(\alpha/2\pi) \int d^3x dt \mathbf{E} \cdot \mathbf{B}$, with α the fine-structure constant and the parameter $\theta = 0$ or π for trivial insulator and TI, respectively [4]. Many novel properties have been proposed as a result of this topological response [4–6], which are interesting in both fundamental physics and device applications. In proximity with an ordinary superconductor, TI also provides a new candidate for topological quantum computation [7].

The first TI was theoretically predicted and experimentally observed in the HgTe quantum well [8, 9]. This work discovered the basic mechanism of band inversion driven by spin-orbit coupling (SOC), which serves as a template for most TIs discovered later. Since then, several TIs in both 2D and 3D have been theoretically proposed and experimentally realized, $\text{Bi}_{1-x}\text{Sb}_x$ alloy [10, 11], the family of Bi_2Se_3 , Bi_2Te_3 and Sb_2Te_3 [12–14], the family of TlBiTe_2 and TlBiSe_2 [15–17]. Many other materials are theoretically predicted and still waiting for experimental verification [18–24]. Of particular interest are the magnetic atom doped topological insulators for the effects of magnetic impurities and ferromagnetism on the topological surface states [25–27]. In this letter, we report a new family of ternary chalcogenides compound LnBT_3 (Ln = rare earth elements, B = Bi, Sb, and T = Te, Se), which share the same crystal structure with Bi_2Se_3 family. LnBT_3 can be regarded as Bi_2Se_3 with

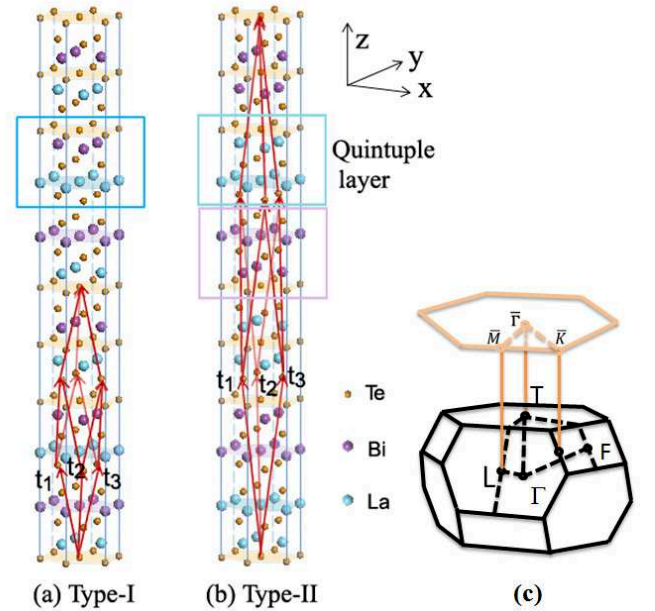


FIG. 1: (Color online) Crystal structures of LaBiTe_3 with three primitive lattice vectors denoted as $t_{1,2,3}$ for (a) type-I and (b) type-II lattices. The quintuple layers, Te-La-Te'-Bi-Te for type-I lattice, and Te-La-Te'-La-Te and Te-Bi-Te''-Bi-Te for type-II lattice are indicated by rectangles. The c axis of equivalent hexagonal lattice is along the z direction. (c) The first Brillouin zone is shown for the rhombohedral lattice as well as the 2D projected surface.

half of the Bi atoms replaced by Ln. Unlike Bi_2Se_3 family, in these materials inversion symmetry is not always preserved. Since lanthanum (La) and Yttrium (Y) have no $4f$ electrons, LaBiTe_3 , YBiTe_3 , LaSbTe_3 and YSbTe_3 are four simplest ternary rare earth chalcogenides which

have been synthesized in experiments[28]. In this work we focus on these four compounds based on *ab initio* calculations, among which we find that LaBiTe₃ is a strong topological insulator. Moreover, La and Y can be replaced by other rare earth elements which have magnetic moments due to the localized *f* electrons. These systems could provide realizations of the topological Mott insulator state[29]. The versatility of rare earth elements will bring us new possibilities beyond Bi₂Te₃ family.

Method and crystal structure- The electronic structures of LaBiTe₃, YBiTe₃, LaSbTe₃ and YSbTe₃ are calculated in the framework of the density functional theory with Perdew-burke-Ernzerhof type generalized gradient approximation(GGA)[30]. For our calculations, both the *Vienna ab initio simulation package*(VASP)[31, 32] with the projected augmented wave method[33] and the BSTATE package[34] with plane-wave pseudo-potential method are employed. We adopt the 12×12×12 k-point grid for self-consistent calculations. The kinetic energy cutoff for the plane wave basis in BSTATE package is fixed to 340 eV. SOC is included in all of our calculation, except in the calculations for the ionic optimization which is confirmed to be insensitive to SOC.

LaBiTe₃, YBiTe₃, LaSbTe₃ and YSbTe₃ share the same rhombohedral crystal structure with the space group $D_{3d}^5(R\bar{3}m)$ (see Ref.28 and references therein). Here we take LaBiTe₃ as an example. Similar to Bi₂Te₃, the crystal consists of triangular layers stacking along [111] direction with A-B-C... order. Five atomic layers form a quintuple layer (QL) with the order of Te-X-Te-X'-Te, where X and X' denote La or Bi organized in certain pattern, as discussed below. Though the lattice parameters have been measured by experiments, up to our knowledge, the relative position between M and M' has not been fully resolved experimentally. Thus we compare the total energy obtained in *ab initio* calculation for different configurations to search for the most stable structure. Our result indicates that the structures with La and Bi separated in different atomic layers are more stable than those with La and Bi mixed in the same atomic layer. There are two structures which have lowest energy. Because the energy difference between the two configurations are very small, in the following we will study both of them separately. (i) Type-I structure consists of stacking quintuple layers along [111] direction, each of which is ordered as Te-La-Te-Bi-Te, as shown in Fig. 1(a). This structure is inversion asymmetric. (ii) Type-II structure consists of stacking pairs of quintuple layers along [111] direction, ordered as Te-La-Te'-La-Te and Te-Bi-Te''-Bi-Te. This structure is inversion symmetric. The experimental lattice constants and optimized atomic coordinates for the two structures are listed in Table I.

Type-I structure. We start by computing the band structures for LaBiTe₃, YBiTe₃, LaSbTe₃ and YSbTe₃ in the type-I crystal structure. As examples, Fig.2 shows

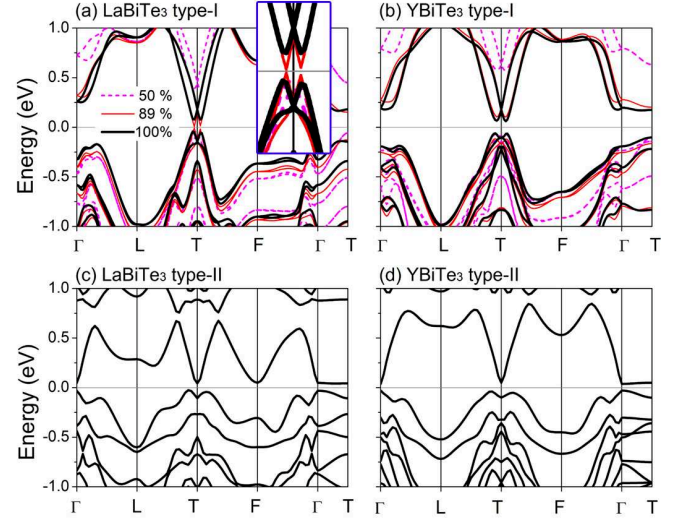


FIG. 2: Band structures for (a) LaBiTe₃ and (b) YBiTe₃ of type-I structures and (c) LaBiTe₃ and (d) YBiTe₃ of type-II structures. The strengths of spin-orbit coupling(SOC) are tuned to be 50% (dashed purple lines), 89% (thin red lines) and 100% (thick black lines) respectively, in (a) and (b). The Fermi energy is set to zero. The energy gap decreases to zero and re-opens as SOC increases from zero to 100% for LaBiTe₃, showing a clear band anti-crossing feature. The Dirac type level crossing at 89% SOC is highlighted in the inset. (e) Brillouin zone for this class of materials. The four inequivalent time-reversal-invariant points are $\Gamma(0;0;0)$, $L(\pi;0;0)$, $F(\pi;\pi;0)$ and $T(\pi;\pi;\pi)$. The surface Brillouin zone is projected from the 3D bulk Brillouin zone into the plane of the atomic layer.

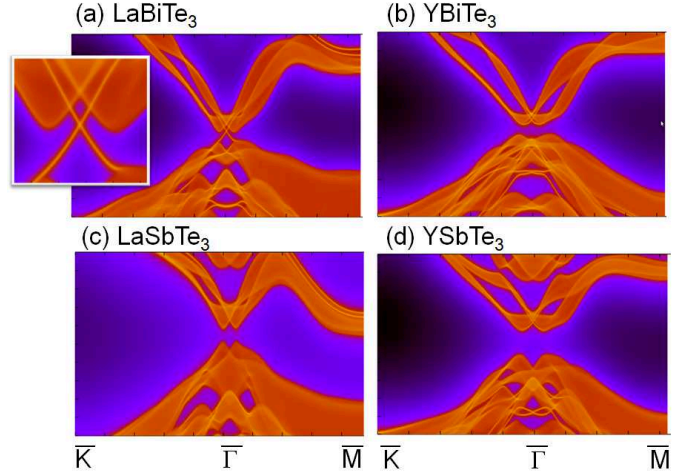


FIG. 3: The band dispersion for an semi-infinite surface of (a) LaBiTe₃, (b) YBiTe₃, (c) LaSbTe₃ and (d) YSbTe₃ of type-I structures. The inset of (a) highlights the surface states near the Dirac cone.

TABLE I: The experimental lattice parameters[28] a and c of hexagonal lattice in unit of angstrom, the theoretically optimized atomic positions and band gaps. Type-II structure has twice the length of type-I along c axis (see Fig.1) and thereafter has double atoms. The atomic coordinate is $(0,0,z_0c)$ in the rhombohedral primitive unitcell. We listed z_0 values for all atoms. These Te atoms as inversion centers of type-II are marked as Te' and Te'' . The energy gap(E_g) is in unit of eV.

	Type-I				Type-II			
	LaBiTe ₃	YBiTe ₃	LaSbTe ₃	YSbTe ₃	LaBiTe ₃	YBiTe ₃	LaSbTe ₃	YSbTe ₃
a	4.39	4.46	4.24	4.47	4.39	4.46	4.24	4.47
c	30.20	31.65	30.40	30.32	60.40	63.30	60.80	60.64
Te(Te'/Te'')	0.0	0.0	0.0	0.0	0.0/0.5	0.0/0.5	0.0/0.5	0.0/0.5
Te	0.20876	0.22243	0.20426	0.21850	± 0.10604	± 0.10764	± 0.10702	± 0.10839
Te	-0.20893	-0.21228	-0.21136	-0.21306	± 0.39572	± 0.38883	± 0.39790	± 0.39076
Bi(Sb)	0.40274	0.40161	0.40102	0.40156	± 0.19922	± 0.19873	± 0.19846	± 0.19801
La(Y)	-0.39938	-0.39416	-0.40111	-0.39582	± 0.29951	± 0.30219	± 0.29913	± 0.30120
E_g	0.12	0.12	0.15	0.28	0.07	0.07	0	0.10

the results for LaBiTe₃ and YBiTe₃. Both of them have similar band gap 0.12 eV around the T point. The band gap of YBiTe₃ is close to the previous experimental value[35] $0.18 \sim 0.23$ eV. As mentioned above, due to the lack of inversion symmetry, the parity criteria for topological insulators[10] does not apply. Alternatively, we study the evolution of conduction and valence bands by tuning the SOC strength artificially. Without SOC, any insulator must be topologically trivial, so that a topological insulator phase can be identified by studying the topological phase transition at some critical SOC strength[8]. A Dirac type level crossing between valence and conduction bands separate the topologically trivial and nontrivial phases.[8, 36] The continuous tuning of SOC is obtained by changing the speed of light c in the VASP package. As shown in Fig.2(a), upon the increase of SOC strength, the band gap of LaBiTe₃ decreases and vanishes on a ring in Brillouin zone (BZ) near T at 89% SOC and opens again, which indicates a topological phase transition[37] and suggests that LaBiTe₃ is a topologically non-trivial insulator with full SOC strength. In contrast, the band gap remains finite upon turning on SOC for YBiTe₃, which is thus a topologically trivial insulator. We perform the same calculations for LaSbTe₃ and YSbTe₃, and find both of them are topologically trivial insulators.

The existence of topological surface states is one of the most important physical consequence of the TIs. To further confirm the topological nature of the proposed materials and study the detailed features of the surface states, we obtain the dispersion of surface states based on *ab initio* method. We construct Tight-binding(TB) Hamiltonian of the semi-infinite system with Maximally localized Wannier functions(MLWF)[38, 39] basis for LaBiTe₃ family materials, and then apply the standard Green function iteration method[40, 41] to obtain the surface density of states. The detail of this method can be found in Ref.36. In Fig.3 we can see clearly that the topological surface states form a single-Dirac-cone at the $\bar{\Gamma}$ point in 2D BZ within the bulk gap for LaBiTe₃, while

no such surface states are observed for YBiTe₃, LaSbTe₃ and YSbTe₃. This result determines the topologically non-trivial nature of LaBiTe₃ without any doubt. From this calculation, we can further obtain the Fermi velocity for LaBiTe₃ to be $4.0 \times 10^5 \text{ m/s}$, similar to that of Bi₂Se₃[12].

Type-II structure. The band structures for LaBiTe₃ and YBiTe₃ of type-II are shown in Figs 2(c) and 2(d). Their band gaps are 0.07 eV near the Γ point, smaller than those of type-I structures. Due to inversion symmetry, we can follow the parity criteria proposed by Fu and Kane[10] to calculate \mathbb{Z}_2 topological index. The product of the parities of the Bloch wave functions are determined for the occupied bands at all time-reversal-invariant momenta $\Gamma(0,0,0)$, $L(\pi,0,0)$, $F(\pi,\pi,0)$, $T(\pi,\pi,\pi)$ in BZ. For LaBiTe₃, we find that the product of parities at Γ is “+” and those at L, F, T are all “-”. Thus LaBiTe₃ is topological nontrivial with \mathbb{Z}_2 index (1;000). For YBiTe₃ and YSbTe₃, we find that the products of parities at Γ, L, F, T are all “-”, so that both of them are topologically trivial with \mathbb{Z}_2 index (0;000). In addition, LaSbTe₃ is found to be a semimetal. For both type-I and -II structures, it is noted that the states near Fermi energy are partially composed by La/Y- $5d_{z^2}$ as well as Bi/Sb- $6p_z$ and Te- $5p_z$ orbitals.

Discussion- In summary, our *ab initio* calculation has verified that LaBiTe₃ is a strong topological insulator. The substitution of La in LaBiTe₃ with other rare earth elements will open a wide platform to study various topological non-trivial behaviors. It is found that many isostructural stoichiometric compounds similar to LaBiTe₃ also exist in the family of ternary rare earth chalcogenides[28], such as LnBiTe₃ (with Ln standing for La, Ce, Pr, ..., Lu or Y) and LnSbTe₃, many of which have intrinsic magnetic moments due to the localized f electrons (e.g. Pr, Sm or Gd). Since the strong correlation effect induced by f electrons can not be properly taken into account in the current GGA calculations, we will leave the detailed study of these materials for the future work but discuss the possible states induced by

strong electron correlation. First, if the coupling between magnetic moments is ferromagnetic, quantum anomalous Hall effect may emerge in thin films or heterostructures of LnBiTe_3 when the band structure is normal for one spin while inverted for the other, similar to the proposals in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ [42] and $\text{Bi}_{2-x}\text{Fe}_x\text{Se}_3$ [27]. Second, if the magnetic coupling is ferromagnetic within one atomic layer but anti-ferromagnetic between two neighboring atomic layers, the dynamical axion field may be realized, which is proposed as a novel optical modulators device[6]. The recently proposed topological Kondo insulator[43] may also exist in this class of materials due to the existence of f electrons. Besides the topological insulators the newly proposed materials have another important potential application. As we have shown, some materials in this family are trivial insulators such as YBiTe_3 and YSbTe_3 . Due to their similarity with the Bi_2Te_3 family, the trivial insulators in this new family are natural candidates of barrier materials for thin films or quantum wells of the TIs in the Bi_2Te_3 family and the new LaBiTe_3 family. Especially, YBiTe_3 ($a=4.46$ Å) - LaBiTe_3 ($a=4.39$ Å) and YBiTe_3 - Bi_2Te_3 ($a=4.3835$ Å)[44] pairs have the best-matched lattice constants. Such a barrier material may help protecting a clean surface of TI and greatly improve the surface condition in transport experiments, which is a main difficulty in the current experiments.

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